
CHAPTER 2 LITERATURE SURVEY

2.1 INTRODUCTION

Over ninety-nine per cent of the element content of the earth's crust is composed of the "major elements" which are O, Si, Al, Fe, Ca, Na, K, Mg, Ti and P. The remainder of the elements in the periodic table are trace elements as their specific concentrations in the earth's crust do not generally exceed 0,1 per cent (1000 mg/kg) (Alloway, 1995). Trace elements can also be referred to as micro-nutrients which are those elements essential for growth and development of organisms (e.g. Zn, Mn, Cu, Fe, Mo and B). However, a micro-nutrient in excessive quantity can be toxic, while non-essential exogenous metals, for example Cd and Hg, are toxic at virtually all concentrations. Heavy metals refer to metallic elements with an atomic weight greater than that of Fe (55,8 g/mol) or to an element with a density greater than 5,0 g/cm³ (Pierzynski, Sims & Vance, 1994). Although trace elements are ubiquitous in soil parent material, soils are contaminated by trace elements due to anthropogenic inputs. According to Alloway (1995), the major sources of anthropogenic trace element inputs are: metalliferous mining and smelting; agricultural and horticultural materials; sewage sludges; fossil fuel combustion; metallurgical industries (manufacture, use and disposal of metals); electronics (manufacture, use and disposal of electronic equipment); chemical and other manufacturing industries; waste disposal, warfare and military training.

2.2 NATURAL CONCENTRATIONS OF TRACE ELEMENTS IN SOILS

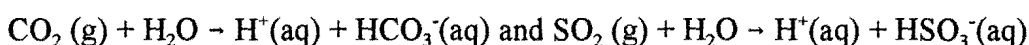
2.2.1 Geochemical origin of trace elements in soils

Trace elements occur in rock forming minerals due to isomorphic substitution or by fixation on free structural sites. Isomorphic substitution refers to the replacement of one of the major elements by a trace element ion in the crystal lattice of the mineral at the time of crystallization.

The substitution is governed by the ionic charge, ionic radius and electronegativity of the major element and the trace element replacing it. Substitution can take place when there is a difference of less than 15 per cent in the radii of the replacing ions and when the charge of the ions do not differ by more than one unit (Bohn, McNeal & O'Conner, 1985). The natural concentration of trace elements in soils is a result of weathering that releases trace elements from their host minerals during soil formation (Kabata-Pendias, 1992).

Soils represent a dynamic chemical system where mineral transformation occurs continuously. Weathering is the basic soil forming process and the degree of weathering that trace element containing primary minerals are subjected to, will therefore influence the lithogenic metal content of soils (Kabata-Pendias & Pendias, 1986). Weathering can be defined as the physical disintegration and chemical decomposition of rocks (Alloway, 1995). Singer & Munns (1992), describes physical weathering as the process which breaks down rocks to smaller particle sizes. Processes such as freezing and thawing, uneven heating, abrasion and shrinking and swelling (due to wetting and drying) break large particles into smaller ones. Plant roots that grow into thin cracks or the formation of salt crystals in cracks, can force joints or cracks open until the rock breaks.

Chemical weathering is the process that changes minerals from their original composition to new minerals and chemical components that are stable and equilibrated in the particular soil environment in the presence of water (Kabata-Pendias & Pendias, 1986). The rates at which these reactions take place are directly related to temperature and water availability, thus chemical weathering is more pronounced in the humid tropics than in cold and dry areas (Alloway, 1995). Water increases the rate of chemical weathering as water contains weathering agents (e.g. CO₂, O₂, organic acids such as humic and fulvic acid, SO₂ (aq), H₂SO₄ and HNO₃) in solution and transports these to chemically active sites on mineral surfaces. Water provides the H⁺ ion to enable acid forming gasses to act as acids:



Rainwater is usually slightly acidic due to the presence of dissolved CO₂, or more acidic due to acid-rain forming agents. Rainwater also lacks alkalinity and the slightly acidic rainwater is chemically aggressive and promotes weathering (Manahan, 1994). Typical chemical weathering reactions include: Dissolution; hydration; dehydration; hydrolysis; oxidation; acid hydrolysis and complexation. These chemical weathering reactions are responsible for the conversion of rock forming minerals to soils. According to White (1995), the rate at which chemical weathering of silicate minerals in the natural environment takes place, depends on a number of factors, including mineral surface reactivity, the role of hydrologic heterogeneity on fluid residence times in soils, soil pH, vegetation and climate.

2.2.2 Pedogenic processes that translocate trace elements in soils

Pedogenesis is defined by Alloway (1995) as the process by which a thin surface layer of soil develops on weathered rock material, gradually increasing in thickness and undergoing differentiation to form a soil profile. The soil profile contains distinct layers (horizons) which differ, according to Jennings, Brink & Williams (1973), in moisture content, colour, consistency, structure, and texture. Soil formation is a function of climate, biological activity, topography, parent material and time (White, 1995).

Soil is a multicomponent system consisting of solid, liquid and gaseous phases as well as living organisms (Bohn *et al.*, 1985). The solid phase is composed of inorganic matter (primary and secondary soil minerals) and organic matter. The liquid phase or the soil solution is a water solution with a composition and reactivity defined by the properties of the incoming water and affected by fluxes of matter and energy originating from the soil solid phase, biological system and the atmosphere. The gaseous phase or the soil atmosphere is composed of the same gases as the atmosphere (CO₂, N₂ and O₂) as well as gases that arise from biological activity (Yaron, Calvert & Prost, 1996).

Natural translocation and accumulation of trace elements in soils are the result of soil processes which include leaching, gleying, podzolization, surface organic accumulation and ferralitisiation (Thornton, 1999).

2.3 BEHAVIOUR OF TRACE ELEMENTS IN SOILS

According to Bourg (1995), the mobility of trace elements in soils depends on a complex network of interactions between aqueous and heterogeneous chemical reactions, as well as physical phenomena such as particle coagulation and flocculation. Bourg (1995), distinguishes between soil chemical reactions that tend to increase trace element mobility in soils (e.g. dissolved inorganic and organic complexation) and reactions that delay trace element availability and transport (e.g. precipitation, adsorption, co-precipitation and sorption).

The soil solution is the medium for these reactions, and the dynamic equilibria reactions which can occur in soils are schematically displayed in Figure. 2.1 after Lindsay (1979) and Sparks (1995). Plants take up ions in the soil solution which can then be redistributed in the food chain (1). These ions are released back to the soil solution when the plants die and decompose (2). Ions in the soil solution can be sorbed on inorganic and organic soil components (3) and these sorbed ions can be desorbed back to the soil solution (4). If the soil solution becomes supersaturated with a certain mineral, this mineral will precipitate (5) and a mineral will dissolve if the soil solution is undersaturated with a mineral, until equilibrium is reached (6). Ions in the soil solution can be transported through the soil to the groundwater or ions can be removed through surface runoff. Upward movement of ions can occur through capillarity, a process driven by evaporation and drying (7 and 8). Micro-organisms can remove ions from the soil solution (9). When these organisms die and organic matter is decomposed, ions are released into the soil solution (10 and 2). Gases may be released to the soil atmosphere in soil pores (11) or become dissolved in the soil solution (12).

while low or negative values indicate the existence of reduced species and the soil is said to be under anaerobic conditions. Oxidic soil conditions range between +300 to +800 mV (pE of 5,1 - 13,5) while reducing soil conditions range between +118 to -414 mV (pE of +2 to -7). The Eh of soil can be measured, but soil colour provide a good indication of the redox status of the soil. Red and bright yellow-brown colours indicate oxidic conditions while blue-green, dull yellow and grey soil colours indicate anaerobic conditions. These colour differences are related to the oxidation state of iron in the soil.

2.5 NATURAL AND PROVOKED MOBILIZATION OF TRACE ELEMENTS IN SOILS AND SEDIMENTS

According to Kabata-Pendias (1992) the affinity of metals to the various soil components governs their mobility. Metals such as Cd and Zn that are generally more mobile, exist mainly as organically bound, exchangeable and water soluble species, while less mobile elements such as Pb, Ni and Cr are mainly bound in silicates or the residual fraction. Copper and Mo occur predominately in organically bound or exchangeable soil fractions. The water soluble, organically bound and exchangeable soil fractions are the most mobile trace element occurrences in soils. Figure. 2.2 depicts the speciation of heavy metals in soils. The mobility of metals in soils is strongly influenced by changing soil environmental conditions.

According to Förstner & Kersten (1988) the solubility, mobility and bioavailability of particle-bound metals can be increased by four main factors in terrestrial and aquatic environments:

1. Lowering of pH. In general most metal cations are most mobile under acid conditions with the exception of Mo that is more mobile under alkaline soil conditions.
2. Increased occurrence of natural or synthetic complexing agents which can form soluble metal complexes that will increase metal mobility.
3. Increasing salt concentrations result in an increase in competition for sorption sites on solid surfaces which increase the release of metals from sorption sites. In addition, Cl

forms soluble chloro-complexes with some trace metals.

4. Changing redox conditions. Hydrrous Mn-, Al- and Fe-oxides will dissolve when placed in a reducing environment, causing the release of co-precipitated metals into the soil solution (Alloway, 1995). According to Bourg (1995) in medium to strong alkaline pH and oxidizing environments, amorphous Fe and Mn oxides in soils are strong adsorbents or co-precipitating matrices. When the environment is only slightly oxidizing, and for medium acidic pH ranges, the surface reactive Fe and Mn oxyhydroxides are solubilized when Fe^{3+} and Mn^{4+} are reduced to soluble species. Thus co-precipitated metals are released. When the pH is slightly alkaline, Fe and Mn may precipitate as carbonates that are less adsorbent than the corresponding oxides.

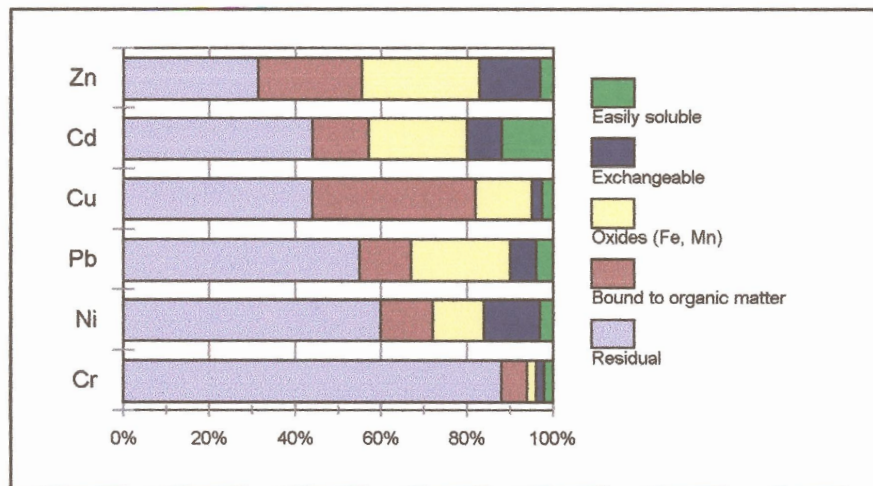


Figure 2.2 Speciation of trace elements in soils as a percentage of total content after Kabata-Pendias (1992)

Förstner & Kersten (1988) summarised the relative mobilities of elements in sediments and soils under changing pH and Eh conditions (Table 2.2). Changes from reducing to oxidizing soil conditions will involve the transformation of sulphide minerals and cause soil pH to decrease. This will increase the mobility of chalcophile elements such as Hg, Zn, Pb, Cu and Cd. The mobility of Mn and Fe on the other hand, is lower under oxidizing conditions.

Table 2.2. Relative mobilities of elements in sediments and soils as function of Eh and pH (after Förstner & Kersten (1988), cf, references therein).

| Relative mobility | Electron Activity | | Proton activity | |
|--------------------|-------------------------------|---------------------------------|----------------------------------|---------------------------|
| | Reducing | Oxidizing | Neutral to alkaline | Acid |
| Very low mobility | Al, Cr, Mo, V, U, Se, S, B | Al, Cr, Fe, Mn | Al, Cr, Hg, Cu, Ni, Co | Si |
| Low mobility | Si, K, P, Ni | Si, K, P, Pb | Si, K, P, Pb | K, Fe(III) |
| Medium mobility | Mn | Co, Ni, Hg, Cu, Zn, Cd | Mn | Al, Pb, Cu, Cr, V |
| High mobility | Ca, Na, Mg, Sr | Ca, Na, Mg, Sr, Mo, V, U, Se | Ca, Na, Mg, Cr | Ca, Na, Mg, Zn, Cd, Hg |
| Very high mobility | Cl, I, Br | Cl, I, Br, B | Cl, I, Br, S, B, Mo, V, U, Se | Cl, I, Br, B |

2.6 TRACE ELEMENT TOXICITY

At least 25 elements are considered essential to life; these include C, H, N, O and macro-nutrients such as Na, K, Mg, S, P, Cl, Si and Fe, of which the majority are metals. This trend also holds for the micro-nutrients that are V, Cr, Mn, Fe, Co, Ni, Ca, Zn, Mo, Se, Fe and I. Trace elements or “heavy metals” refer to micro-nutrients and other non-essential elements that have low natural environmental concentrations. The micro-nutrients are essential to growth but a micro-nutrient in excessive quantity can be toxic, while non-essential exogenous metals, for example Hg, are toxic at virtually all concentrations (Crouse *et al.*, 1983). Any trace element can have an adverse effect on any organism if the dose is high enough. The biological function, phytotoxicity and mammalian toxicity character of some trace elements are presented in Table 2.3.

According to McBride (1994) the elements listed in Table 2.3 that are more toxic to animals than plants (e.g. As and Pb) present the most insidious hazard to human health as these elements may accumulate in plants to concentrations that are toxic to animals or humans while the plants do not display any signs of phytotoxicity. The toxicity rating in Table 2.3 is dependant on the actual likelihood or frequency of toxicity in the natural environment. For example, Mn has a low toxicity to plants but Mn- induced phytotoxicity (commonly occurring as high Mn^{2+} concentrations) can develop in wet soils. In comparison, Cr and Pb have a higher phytotoxicity rating but they are usually very insoluble in soils so that these elements rarely induce toxicity.

Table 2.3 Biological function and toxicity of some trace elements (after McBride 1994)

| Element | Biological Function | Phytotoxicity | Mammalian Toxicity |
|---------|---|---------------------------------|--|
| As | None known in animals. Constituent of phospholipid in algae and fungi | Medium - High (5 - 20 ppm) | High |
| Co | Essential for animals. Co-factor in many enzymes. Plays a role in symbiotic N_2 fixation. | Medium - High (15 - 50 ppm) | Medium |
| Cr | May be involved in sugar metabolism in mammals | Medium - High (5 - 30 ppm) | Cr^{6+} High while Cr^{3+} Medium |
| Cu | Essential to all organisms. Co-factor in redox enzymes, O_2 transport | Medium - High (20 - 100 ppm) | Medium |
| Ni | None known in animals. May be essential to plants. Found in urease enzyme. | Medium - High (10 - 100 ppm) | Medium |
| Pb | None known | Medium (30 - 300 ppm) | High (cumulative poison) |
| Zn | Essential to all organisms. Co-factor in numerous enzymes | Low - Medium (100 - 400 ppm) | Low - Medium |

Values in parenthesis are concentrations of element in leaf tissue that show toxicity in plants that are neither highly sensitive or tolerant.

2.7 GEOCHEMICAL BEHAVIOUR OF CERTAIN TRACE ELEMENTS

This section is a discussion of the abundance in soils and geochemical behaviour of the trace elements considered in this study. The following discussion borrows heavily from McBride (1994) and Alloway (1995).

2.7.1 Arsenic

Mean arsenic concentrations in soils range from 2,2 - 25 ppm worldwide. Arsenic occurs in soils in the +3 and +5 oxidation state, although -3 and 0 oxidation states are possible in strongly reduced soils and sediments. Arsenate (+5), as AsO_4^{3-} , represents the oxidized state and occurs in aerobic soils, while arsenite (+3), which takes forms such as $\text{As}(\text{OH})_3$ and AsO_3^{3-} , is stable in anaerobic soils.

The chemical behaviour of arsenate is similar to that of phosphate in soils as it is likely to be adsorbed by Fe, Mn and Al oxides, noncrystalline aluminosilicates and, to a lesser extent, layer silicates. Arsenate adsorbs most effectively at low pH values and has therefore a low mobility in acid soils with a high clay or oxide content. However, in neutral to alkaline soils, especially if the soils are sodic, As may be mobile in the form of soluble Na arsenate. The oxidation of arsenite to arsenate is promoted by the presence of microbes and Mn oxides.

Arsenite adsorbs less effectively in alkaline soils than arsenate in acid soils, adsorption being most effective in soil pH ranging from 7 to 9. If oxic soils are subjected to anaerobic conditions, both co-precipitated or adsorbed arsenate and arsenite can be released into the soil solution by the dissolution of Fe and Mn oxides. Desorbed arsenate is then reduced to arsenite which is eventually converted to insoluble forms, causing As mobility first to increase and then to decrease if anaerobic conditions are maintained. When soils remain anaerobic for long periods, sulphides, formed under reducing soil conditions, may co-precipitate As in its lower oxidation state. Volatile alkylarsene($(\text{H}_3\text{C})_3\text{AsO}$) compounds may also form under these conditions causing, a

loss of As to the atmosphere or to air-filled soil pores.

2.7.2 Cobalt

Mean cobalt concentrations in soils range from 1,6 - 21,5 ppm worldwide. Cobalt occurs in soils in the +2 and +3 oxidation state. Co^{2+} is the dominant form in the soil solution. Cobalt preferentially associates with Fe and Mn oxides due to sorption and co-precipitation. Cobalt is strongly sorbed on Mn-oxides where Co^{2+} is oxidized to Co^{3+} , which results in a low mobility of Co in oxidized soils. Cobalt is usually found in association with Mn-oxides in soils where Co can replace Mn in the oxide structure. Under neutral soil conditions cobalt is less mobile than under acid soil conditions due to increased sorption of Co on oxides, silicate clays and organic matter, and possibly the precipitation of $\text{Co}(\text{OH})_2$. Under strongly reducing conditions, the precipitation of Co-sulphides may inhibit mobility.

2.7.3 Chromium

Mean Cr concentrations in soils range from 7 - 221 ppm worldwide. Chromium occurs in soils in the +3 (chromic) and +6 (chromate) oxidation state. Cr^{3+} is the dominant form in the soil solution. The chromic cation is very immobile in soils as it complexes strongly with soil organic matter and sorbs even at relatively low pH values on oxides and silicate clays. In Fe-oxides, Cr^{3+} can replace Fe in the crystal lattice, and in higher soil pH conditions, $\text{Cr}(\text{OH})_3$ precipitates, both processes reducing mobility. If the soil is not exceedingly acidic, the Cr^{3+} form is very immobile in soils and thus the insoluble Cr^{3+} form dominates in most soil types, and it generally occurs as insoluble hydroxides and oxides.

The mobility and bioavailability of the chromate ion (CrO_4^{2-}) in soils is higher, as chromate is less strongly adsorbed by soil constituents. The chromate ion is very toxic and is stable at higher soil pH values, but generally most Cr^{6+} is spontaneously reduced to Cr^{3+} under acid soil conditions in the presence of soil organic matter, as the organic material provides complexing groups which

stabilise the chromic form. This reduction occurs more rapidly in acid soils than in alkaline soils.

2.7.4 Copper

Mean Cu concentrations in soils range from 6 - 80 ppm worldwide. Copper mainly occurs in soils as the divalent Cu^{2+} cation, although reduction of Cu^{2+} (cupric) to Cu^+ (cuprous) and Cu^0 (metallic copper) can occur in reducing conditions, particularly when stabilizing halide or sulphide ions are present.

Copper has a low mobility in reduced soils as the element is chalcophile, and forms insoluble minerals such as Cu_2S and CuS . In oxic soils, Cu^{2+} is also relatively immobile as copper is easily adsorbed on most colloidal soil material (e.g. Mn-, Fe- and Al-oxides, silicate clays and humus). Adsorption increases with increasing soil pH. Above a pH of 6, precipitation of malachite or azurite may occur in soils with a sufficient Cu concentration. Organically bound Cu^{2+} is the least mobile of all organically bound divalent transition metals. Copper is rated to have a low mobility in near-neutral soils as the high-affinity of soil colloids for Cu^{2+} reduces the concentration of the element in the soil solution. In more alkaline soils, the mobility of copper may become significant due to the formation of soluble complexes of Cu^{2+} (hydroxy, carbonate and organic matter complexes) which are adsorbed to a lesser degree.

2.7.5 Nickel

Mean Ni concentrations in soils range from 4 - 55 ppm worldwide, The Ni^{2+} oxidation state is the only stable form of nickel in the soil environment. The Ni^{2+} cation is comparable in geochemical behaviour with Cu^{2+} , except that it is slightly less electronegative than Cu^{2+} . However, nickel is several times more phytotoxic than Cu. Nickel is the smallest divalent transition metal cation and fits easily into octahedral sites of silicate clays and co-precipitates readily into Mn- and Fe-oxides. Nickel also bonds preferentially with soil organic matter and bio-accumulation of Ni in organic rich soils is pronounced. The mobility of Ni is rated as medium

in acid soils but very low in neutral to alkaline soils, as Ni sorption on oxides, noncrystalline aluminosilicates and clay minerals increases above pH 6. Under reducing soil conditions Ni has a restricted mobility since Ni^{2+} is incorporated into sulphides.

2.7.6 Lead

Mean Pb concentrations in soils range from 10 - 84 ppm worldwide. Lead exists principally in the Pb^{2+} oxidation state in soils. Lead is the least mobile heavy metal in soils, particularly under reducing or non-acid soil conditions. Lead is a strongly chalcophile element and is very immobile in reducing soil conditions as lead precipitates as insoluble sulphide compounds. In oxic soils, Pb solubility decreases with increasing pH, since at higher pH levels, complexation of Pb with organic matter, sorption of Pb on oxides and clays and precipitation of Pb-carbonate, -hydroxide or -phosphates, are favoured. Manganese oxides in soils may also oxidize Pb^{2+} to the even less soluble Pb^{4+} ion which will further reduce the mobility of lead in oxic soils. Lead complexes strongly with soil organic matter and when introduced to soils, will bio-accumulate in organic rich topsoil. In alkaline soils however, the mobility of lead may be slightly increased due to formation of Pb-organic or Pb-hydroxy complexes.

2.7.7 Zinc

Mean Zn concentrations in soils range from 17 - 125 ppm worldwide. Zinc exists only in the Zn^{2+} oxidation state in soils. Zinc is the most mobile and soluble trace metal cation under acidic, oxic soil conditions, as Zn^{2+} is held in exchangeable forms on soil organic matter and clays. However, the mobility of zinc in neutral soils is significantly lower, since sorption on oxides and aluminosilicates as well as complexation with soil organic matter, lowers the solubility of zinc. Zinc is not known to co-precipitate into octahedral sites of oxides and silicates. In alkaline soils, the mobility of zinc may increase since soluble Zn-organo and Zn-hydroxy anions may form. But if Zn is present in sufficient concentration, insoluble Zn-oxide, hydroxide or hydroxycarbonate precipitates will restrict the mobility of zinc. In anaerobic soils, the release of Zn^{2+} from dissolved

Fe and Mn oxides may at first increase Zn mobility, but the mobility will finally be restricted by the precipitation of exceedingly insoluble ZnS.

2.8 LEACHING TECHNIQUES

Soils consist of a heterogeneous mixture of different organic substances, quartz, primary and secondary alumino-silicate clay minerals, Fe-, Al- and Mn-oxides and other solid components, as well as variety of soluble substances. The binding mechanisms of trace elements in soils are many, and vary with the composition of the soil, the soil pH and the redox conditions particular to the soil. The complexity of possible reactions, and often unknown reaction kinetics in natural soil systems, restricts studies of trace element distribution in the solid soil phase to operationally defined analytical procedures (Brümmer, Gerth & Williams 1986). To assess the reactivity of the species or binding forms of heavy metals in solid materials, different procedures involving sequential extraction techniques have been developed from the original method proposed by Tessier, Campbell & Bisson (1979). These techniques assume that the following trace element species exist in soils: Water soluble (in the soil solution); exchangeable; organically bound; occluded in iron and manganese oxides; definite compounds (e.g. trace element carbonates, phosphates, sulphides); and structurally bound in silicates (the residual fraction).

According to Coetzee, Gouws, Plüddemann, Yocoby, Howell and Drijver (1995), sequential extraction procedures have received adverse critique and controversy in literature over the last decade. The main reasons being that the techniques are used in a nondiscriminatory way with the assumptions (i) that the procedures are selective, (ii) that phase exchanges do not occur and (iii) that matrix effects can be ignored. However various authors have shown that these assumptions can not generally be made.

The water soluble fraction, together with the exchangeable soil fraction, represents the mobile portion of trace elements in soils (Brümmer *et al.*, 1986). The other fractions are essentially immobile and the mobilisation of these bound species is controlled by reaction kinetics. The

mobile fraction of trace elements in soils represents the bioavailable portion and leaching techniques such as the 1M NH_4NO_3 technique used by Schloemann (1994), therefore result in extracted ion concentrations that can be correlated with the amount of ions held on charged soil surfaces (e.g. clays, oxides and humus).

2.9 SOIL STANDARDS

Environmental policies governing air and water quality were developed before soil protection became an important issue in the European Union. One of the reasons for this may be that the effects of poor air and water quality are plainly visible, while the effects of soil pollution can remain unnoticed for a long time. Often the effects of bad or dangerous soil quality become apparent during changes in land use (Vegter, 1995).

According to Ferguson, Darmendrail, Freier, Jensen, Jensen, Kasamas, Urzelai & Vegter (1998), most industrialised countries are currently drawing up or revising policies and procedures that deal with contaminated land. These policies contain screening and guideline values that are used to assess whether a soil is polluted or not. Screening values are defined as generic values intended to screen out those sites (or parts thereof) for which risks are too small to warrant more detailed investigation. These values tend to be based on very pessimistic exposure assumptions and/or very stringent criteria for maximum tolerable risk. Guideline values are designed to provide generic guidance to risk assessors on the significance of contaminant concentration in soils or other media. Debate around the usefulness of both screening and guideline values has centered around the reliability of the calculated values, the treatment of uncertainty and the relationship between generic scenarios and real site conditions. The advantages of using generic values are listed below:

- speed and ease of implementation, and similar sites would be handled in a similar way;
- useful for initial assessment of significance of contamination;
- encourage planners and developers to undertake decontamination/restoration;

- reality of contaminated land made understandable for the lay person;
- facilitate environmental audits for industrial/mine sites;
- facilitate monitoring/permitting of operational industrial/mine sites;
- can be used in performance assessment of soil treatment plants;
- imply non-negotiability and reduce local political influences.

2.9.1 Screening values

Steyn, Van der Watt & Claassens (1996) summarised the screening values which apply to South Africa and some other countries (Table 2.4). These values are used to assess whether a soil is contaminated and represent the total concentration of an element in the < 2 mm fraction of a soil.

Table 2.4 Maximum permissible total soil concentrations of some trace elements used in legislation or in guidelines for various countries as summarized by Steyn *et al.* (1996). All values are in mg/kg dry soil for the < 2 mm soil fraction.

| | South Africa | Australia/ New Zealand | Germany | United Kingdom | Switzerland |
|-----------|--------------|------------------------|---------|-------------------|-------------|
| Cd | 2 | 3 | 1.5 | 3 | 8 |
| Co | 20 | - | - | - | 25 |
| Cr | 80 | 50 | 100 | 400 (provisional) | 75 |
| Cu | 100 | 60 | 60 | 135* | 50 |
| Hg | 5 | 1 | 1 | 1 | - |
| Ni | 15 | 60 | 50 | 75* | 50 |
| Pb | 56 | 300 | 100 | 300 | 50 |
| Zn | 185 | 200 | 200 | 300* | 200 |
| As | 2 | 20 | - | 50 | - |

* Permissible concentration for soil pH 6,00 - 7,00

2.9.2 Guideline values

Examples of guideline values which comment on the significance of a contaminant concentration in soil are shown in Table 2.5.

Table 2.5 Recommended maximum NH_4NO_3 extractable threshold concentration (mg/l) that should not be exceeded in the soil (from Schloemann (1996), after Prüeß, Turian & Schweikle 1991).

| | Recommended maximum extractable concentrations (mg/l in soil fraction < 2mm) | Impacted soil functions and ranking of concerns | | | | |
|----|--|--|---|--------------------|----------------------------|---|
| | | Pollutant buffer with regard to plants for human consumption | Pollutant buffer with regard to plants for animal consumption | Habitat for plants | Habitat for soil organisms | Pollutant filter with regard to groundwater |
| As | 1 | PC | X | C | X | C |
| Be | 2 | X | X | X | X | INV |
| Bi | 1 | X | INV | X | X | X |
| Cd | 2 | PC | C | X | C | C |
| Co | 5 | X | C | C | X | X |
| Cr | 1 | X | X | X | PC | C |
| Cu | 2 | X | C | C | PC | C |
| Ni | 1 | X | X | C | X | X |
| Pb | 2 | PC | C | X | C | C |
| U | 4 | X | X | X | X | INV |
| V | 1 | X | X | INV | X | X |
| Zn | 10 | X | X | C | X | X |

PC = primary concern, C = concern, INV = further investigations needed to assess risk. X = limited soil functioning only if the maximum concentration is excessively exceeded

2.10 RISK ASSESSMENT OF METAL POLLUTION IN SOILS

Pierzynski *et al.* (1994) define risk as the probability or chance of injury, loss or damage and can be applied to contaminated soils which represent a risk to humans and other organisms as a result of the concentration of pollutants in soils. According to Ferguson *et al.* (1998) risk assessment is an objective way of assessing the impact of polluted soil on human health, ecosystems and the general environment. Risk assessment usually involves a detailed investigation of all sources, pathways and receptors of concern at a site. This process is lengthy and costly, and therefore a tiered approach in investigating a site is followed. The risk assessment procedure is a systematic approach for estimating the probability that site-specific hazards are realized. Firstly, the assimilated data and information obtained from site investigations are used to conduct a baseline risk assessment whereby contaminants of potential concern are detected and the significance of their presence is established in terms of human health and environmental risk. This process requires an assessment of the site by modelling site specific exposure routes through source-path-target substantiation and analysis. The results of a base line risk assessment can be used to decide on the requirements for monitoring, further investigations or remediation measures, if required.

2.10.1 Exposure assessment

Pierzynski *et al.* (1994) define exposure assessment as the procedures by which the identity of the organisms exposed to a soil contaminant is determined. The relative contribution of each route of exposure to the dose of the recipient is also determined. The dose refers to the amount of contaminant ingested or inhaled by the receptor organism. Various organisms can receive a dose in different ways, for example, humans and animals can be dosed via inhalation, by ingestion or by dermal contact with harmful soil contaminants. Plants on the other hand are dosed by extracting contaminated soil water, by respiration with contaminated air or by adsorbing particulate pollutants on the waxy surfaces of leaves. Ferguson *et al.* (1998) list some of the routes by which contaminants may be transported as soil, groundwater, surface water, dust, uptake or adsorption by plants and aerosols. Contaminants may undergo transformation through

biological, chemical or physical means when *en route* to the receptor which may affect its toxicity, availability or mobility. Various models may be used to model the ultimate dose to a receptor group and this concentration is used to perform a dose - response analyses in order to characterise the risk to a receptor. The complexity of exposure routes that needs to be considered when performing a risk assessment investigation on a contaminated site, is indicated in Figure.2.3.

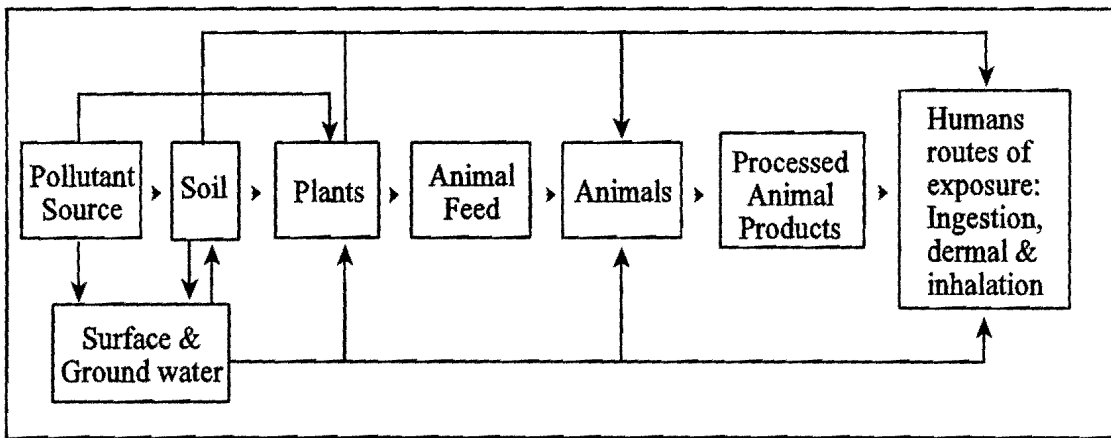


Figure. 2.3 Some human exposure pathways to be considered when performing a risk assessment investigation of a heavy metal contaminated site (after Pierzynski *et al.*, 1994).

2.11 ACID MINE DRAINAGE

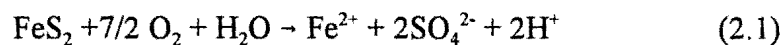
The uncontrolled release of acid mine drainage (AMD) is perhaps the most serious impact that mining can have on the environment (Ferguson & Erickson, 1988). In addition to low pH (i.e. high acidity) acid mine drainage often contains dissolved trace elements in toxic concentrations. The high acidity of mine drainage arises from the rapid oxidation of sulphide minerals. AMD may occur anywhere where sulphide minerals are exposed at the earth's surface (e.g. road cuts or quarries), but metal mines where economically recoverable metals often occur in orebodies of concentrated metal sulphides (e.g. pyrite, FeS₂; chalcopyrite, CuFeS₂ or sphalerite, ZnS) are the primary source of AMD.

The generation of AMD is controlled by a series of factors that may be categorized as primary, secondary, tertiary and downstream factors (Ferguson & Erickson, 1988). Primary factors are those directly involved in the acid production process. Secondary factors control the consumption or alteration of the products of the acid generation reactions. The tertiary factors are the physical aspects of the waste material or mine site that influence the acid production, AMD migration and consumption. Downstream factors control the precipitation of Fe and other metals in rivers and streams into which AMD is discharged. These factors control the quality (including trace element content) of AMD affected water that emanate from a site.

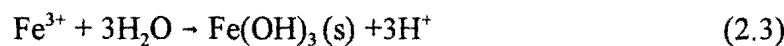
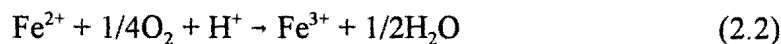
2.11.1 Primary Factors

The reactions of acid generation from sulphide minerals are discussed according to the three-stage stoichiometric example of pyrite oxidation after James (1997) and Ferguson & Erickson (1988) in which one mole of pyrite oxidises to form two moles of sulphate and two moles of H⁺:

Reaction 2.1, represents the oxidation of pyrite to form dissolved ferrous iron, sulphate and hydrogen. This reaction can occur abiotically or can be bacterially catalysed by the bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*.

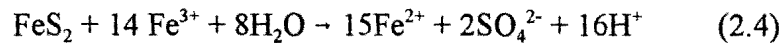


The ferrous iron, (Fe²⁺) may be oxidised to ferric iron, (Fe³⁺) if the conditions are sufficiently oxidising, as illustrated by reaction 2.2. Hydrolysis and precipitation of Fe³⁺ may also occur, shown by reaction 2.3. Reactions 2.1, 2.2 and 2.3 predominate at pH > 4,5.



Reactions 2.1 to 2.3 are relatively slow and represent the initial stage in the three-stage AMD-

formation process. Stage 1 will persist as long as the pH surrounding the waste particles is only moderately acidic ($\text{pH} > 4,5$). A transitional stage 2 occurs as the pH declines and the rate of Fe hydrolysis (reaction 2.3) slows, providing ferric iron oxidant. Stage 3 consists of rapid acid production by the ferric iron oxidant pathway and becomes dominant at low pH, where the Fe^{2+} (ferric iron) is more soluble (reaction 4):



Without the catalytic influence of bacteria, the rate of ferrous iron oxidation in an acid medium would be too slow to provide significant AMD generation. As such, the final stage in the AMD generation process occurs when the catalytic bacteria has become established. Reactions 2.2 and 2.4 then combine to form the cyclic, rapid oxidation pathway chiefly responsible for the high contamination loads observed in mining environments.

2.11.2 Limiting factors

Oxygen is an essential reactant in the formation of AMD and determines the oxidation of sulphide minerals as well as the activity of aerobic autotrophic bacteria. The replenishment of oxygen within a mining waste from the atmosphere is required to sustain the rapid bacteriologically catalysed oxidation processes. Significant oxidation may not occur if the oxygen concentration around the sulphide mineral drops to below 1 to 2 per cent (Ferguson & Erickson, 1988).

Water acts as a reactant, a reaction medium and as a product transport medium in the AMD generation and transport process (Ferguson & Erickson, 1988). Bacterial activity may also be limited by the availability of water. The different forms of pyrite present different activities that then affect the rate of the oxidation reaction. Isometric pyrite may not be as reactive as orthorhombic marcasite or hexagonal pyrrhotite.

the world's acidic drainage. During AMD, Fe-sulphide minerals generate acid which leads to the further dissolution of other Fe-sulphides and their associated mineral assemblages. Examples of chalcophile trace elements associated with common sulphide minerals are presented in Table 2.6. The various metals released to solution are important contributors to environmental degradation. Among the elements that are most widely encountered as potentially toxic pollutants occurring in mine wastes, are Zn, Pb, Cu, Ni, Cd, Hg, Mo, As and occasionally Cr, Co and Se. The potential threat to the environment by elements is evident in countries like Canada where effluent discharged from metal mine tailings must comply with regulatory standards: The maximum monthly mean concentrations (in mg/l) are as follows: As < 0,5; Cu < 0,3; Pb < 0,2; Ni, < 0,5 and Zn < 0,5. The total soluble metal concentration in the effluent must be less than 25 mg/l.

Table 2.6 Common ore minerals of non-ferrous metals and their associated trace elements, compiled by Alloway (1995).

| Metal | Ore minerals | Associated trace elements |
|-------|---|--|
| As | FeAsS, AsS Cu ores | Au, Ag, Sb, Hg, U, Bi, Mo, Sn, Cu |
| Cr | FeCr ₂ O ₄ | Ni, Co |
| Cu | Native Cu, CuFeS ₂ , Cu ₃ FeS ₄ , Cu ₂ S, Cu ₃ AsS ₄ , CuS | Zn, Cd, Pb, As, Se, Sb, Ni, Pt, Mo, Au, Te |
| Ni | (Ni,Fe) ₉ S ₈ , NiAs, (Co, Ni) ₃ S ₄ | Co, Cr, As, Pt, Se, Te |
| Pb | PbS | Ag, Zn, Cu, Cd, Sb, Tl, Se, Te |
| Zn | ZnS | Cd, Cu, Pb, As, Se, Sb, Ag, Au, In |

2.11.7 Environmental affects of gold mine tailings in South Africa

In a study of a number of gold mine tailings dams in the Gauteng province, Marsden (1986) concluded that tailings dams of 20 years and older, have an oxidised zone where leachable sulphate (and associated low pH water and other toxic substances) are virtually absent. He supports this conclusion by the fact that grass and other vegetation grows on many discard

dumps. Through hand auger and test pitting, the thickness of this zone has been established to be ± 10 m in sand dumps and 2 - 3 m in slimes dams (Marsden 1986).

Blight & du Preez (1997) studied the escape of acid and soluble salt pollution from decommissioned gold mine tailings dams and confirmed the presence of the oxidised tailings zone on the surface of slimes dams. The rate of formation of this zone is greater than the rate of erosion from the dam, and consequently they predict that little pollution enters the environment as a result of physical redistribution of tailings. However, when erosion gulleys, that cut through the oxidised zone, develop on the sides of some tailings dams, acid leachate can escape much easier from the tailings impoundments. Marsden (1986) found that sulphate concentrations in soils surrounding gold mine tailings deposits, where tailings had been allowed to wash onto adjacent land, were on average 0,05 per cent (maximum of 0,25 per cent) up to a depth of 2,00 m.

Rösner *et al.* (1998) summarised the results of research on the environmental effects of South African gold mine tailings. Trace element concentrations in water and sediments were analyzed in the 1970's and it was found that elevated concentrations of Co, Cu, Fe, Mn, Ni and Zn are present in stream systems affected by AMD (Förstner & Wittmann, 1976). Funke (1985) concluded that slimes dams contributed approximately 2 per cent of the total salt load entering the Vaal Barrage system. Marsden (1986) concluded that mine dumps older than 20 years make no significant contribution to the current pollution load on aquatic systems, as these tailings dams are often depleted in sulphur bearing minerals in the oxidised zone. Funke (1990) concluded that the amount of sulphur in mine dumps that still oxidizes at present, is low, particularly when compared with the pollution load deriving from mine pumpage and metallurgical plant operation. Evans (1990) found trace element pollution caused by AMD generation in a wetland adjacent to a tailings dam. Walton, Verhagen & Taussig-Duthe (1993) attributed elevated sulphate and metals (Ni, Cu, Fe) concentrations in both, surface and groundwater systems in the Gauteng region to AMD from tailings dams. Znatowicz (1993) found high concentrations of toxic metal (e.g. As, Cd, Ti, V and U) in water and sediment samples downstream from a gold tailings dam.

Coetzee (1995) detected significant radiometric anomalies in selected drainage systems of the Gauteng Province and attributed these to AMD from tailings dams. Pulles, Heath & Howard (1996) stated that seepage released from various waste deposits such as mine dumps was identified as the most significant pollution source with regard to the deterioration of water quality in Gauteng. Rösner (1996) found significant concentrations of As, Cr, Ni, Pb, V and Zn in the oxidized zone of a number of gold mine tailings dams in Gauteng.